HYDROGENATION OF ETHYLENE ON A Co–Mo/Al₂O₃ CATALYST UNDER TRANSIENT CONDITIONS

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Hydrogenation of ethylene on a Co–Mo/Al₂O₃ catalyst at 353 K and atmospheric pressure has been studied. The unsteady-state method was used, in which reactor feed-rate and feed-composition were changed in a defined way. The analysis of transient response curves proved negligible adsorption of hydrogen and ethane and confirmed the reaction mechanism of ethylene hydrogenation which involves reaction of adsorbed ethylene with hydrogen from gas phase in the rate determining step. Combined stationary and transient experimental data were used to calculate kinetic parameters: rate constant of ethylene hydrogenation, total concentration of active sites on the catalyst surface and equilibrium adsorption coefficient of ethylene.

Discrimination between rival kinetic models based on data obtained by steady-state measurements results frequently in a group of statistically indistinguishable kinetic equations. In such a case, one needs additional independent experimental information that can be obtained *e.g.* by the study of reaction under transient (unsteady--state) conditions. Transient experimental data can provide valuable information concerning not only the decision between rival models but also the determination of adsorption properties of reaction components under catalytic reaction conditions.

In the present work we report on the hydrogenation of ethylene on commercial cobalt–molybdenum catalyst CHEROX 36 − 01 which was performed in a continuous flow stirred tank laboratory reactor (CSTR) at 353 K and atmospheric pressure.

THEORETICAL

Hydrogenation of ethylene on cobalt–molybdenum catalyst. Previous kinetic studies[1,2] of ethylene hydrogenation on CHEROX 36 − 01 catalyst showed that the rate of ethylene consumption can be expressed by the equation

$$-R_{\mathrm{E}} = k_{\mathrm{E}} K_{\mathrm{E}} p_{\mathrm{E}} p_{\mathrm{H}} / (1 + K_{\mathrm{E}} p_{\mathrm{E}}) , \qquad (1)$$

which was derived for the case that adsorption of hydrogen and of ethane is negligible and adsorbed ethylene reacts with hydrogen from gas phase in the rate determining step.

Balance equations. Quantitative evaluation of experimental data is based on the material balance of unsteady-state catalytic reactor. For negligible adsorption of at least one reaction component, the material balance procedure can be used to determine concentrations of components adsorbed on the catalyst surface under steady-state reaction conditions[3].

Let us suppose that hydrogenation of ethylene (Eq. *(2)*)

$$C_2H_4 + H_2 \rightarrow C_2H_6 \tag{2}$$

takes place in a continuous flow stirred tank reactor. At time $t = 0$, the feed composition is step-changed and the new steady-state is achieved at time $t = t_s$. The material balance of the transient period (*i.e.* for $t \in \langle 0, t_s \rangle$) has the following form

$$F_i^0 t_s - \int_0^{t_s} F y_i \, dt + W \int_0^{t_s} R_i \, dt + cV(y_{io} - y_{is}) + W(q_{io} - q_{is}) = 0, \quad i = A, E, H, \tag{3}$$

where F_i^0 is the molar feed-rate of component A_i into the CSTR and F is the total molar flow-rate of the reaction mixture out of the reactor, y_{io}, y_i and y_{is} are mole fractions of component A_i at the start, in the course and at the end of the transient period, respectively, R_i is the rate of formation of component A_i, W is the catalyst weight, V is the reactor free volume, c is the total molar concentration of reaction mixture, and q_{io}, q_{is} are the surface concentrations of adsorbed component A_i at the start and end of the transient period, respectively.

The molar flow-rate out of the reactor, F, is not constant during the transient period. The time dependence of F can be determined from dynamic balance equations of the CSTR gas phase

$$F_i^0 + W a_i r = F_i + cV(dy_i/dt), \quad i = A, E, H, \tag{4}$$

where r is the reaction rate, a_i is the stoichiometric coefficient of component A_i ($a_E = a_H = -1$, $a_A = 1$). If one of the starting reaction components (ethylene or hydrogen) is chosen as the key component ($i = k$, $a_k = -1$), the following equation can be written for the isobaric reactor[4]

$$F = \left(F^0(1 - y_k^0) + cV(dy_k/dt) \right)/(1 - y_k), \tag{5}$$

where y_k^0, y_k are mole fractions of the key component in the feed and outlet of the reactor, respectively, and F^0 is the total molar feed-rate into the CSTR. Eq. *(5)* expresses the desired time dependence of molar flow rate at the reactor outlet, $F(t)$, which can be substituted into the second term of balance equations *(3)*.

From the reaction stoichiometry (2) it follows that the rates of formation, R_i, are interrelated as follows

$$R_A = -R_E = -R_H .\qquad(6)$$

In the case of ethylene hydrogenation on the $Co–Mo/Al_2O_3$ catalyst, hydrogen adsorption can be neglected[1,2] and thus

$$W(q_{Ho} - q_{Hs}) = 0 .\qquad(7)$$

Combination of Eqs (3), (6), and (7) gives the simplified balance equations

ethylene:

$$F_E^0 t_s - \int_0^{t_s} F y_E \, dt + W \int_0^{t_s} R_H \, dt + cV(y_{Eo} - y_{Es}) + W(q_{Eo} - q_{Es}) = 0 ;\qquad(8)$$

hydrogen:

$$F_H^0 t_s - \int_0^{t_s} F y_H \, dt + W \int_0^{t_s} R_H \, dt + cV(y_{Ho} - y_{Hs}) = 0\qquad(9)$$

and ethane:

$$F_A^0 t_s - \int_0^{t_s} F y_A \, dt - W \int_0^{t_s} R_H \, dt + cV(y_{Ao} - y_{As}) + W(q_{Ao} - q_{As}) = 0 .\qquad(10)$$

The set of balance equations (8)−(10) contains three unknown terms:

$W \int_0^{t_s} R_H \, dt$, $W(q_{Eo} - q_{Es})$ and $W(q_{Ao} - q_{As})$. The other terms include only directly measurable quantities, and the total molar flow-rate at the CSTR outlet, F, is given by Eq. (5).

If the feed is step-changed from pure hydrogen to reaction mixture containing hydrogen and ethylene, then $q_{io} = 0$ $(i = A, E)$. The set of three balance equations (8)−(10) then includes three unknown parameters $\int_0^{t_s} R_H \, dt$, q_{Es}, and q_{As}. Similarly, if the feed is step-changed from a mixture containing hydrogen and ethylene to pure hydrogen, $q_{is} = 0$ $(i = A, E)$, and the set of balance equations (8)−(10) includes the unknowns $\int_0^{t_s} R_H \, dt$, q_{Eo}, and q_{Ao}. In both cases, surface concentrations of ethylene and ethane under reaction conditions, q_{Es} and q_{As}, can be determined. These surface concentrations correspond to equilibrium between the amount of compound adsorbed on catalyst surface and the gas-phase composition in the steady-state following the transient period.

EXPERIMENTAL

Catalyst. According to the producer (Chemical Works, Litvínov), the cobalt–molybdenum catalyst CHEROX 36-01 contains 14·1% MoO$_3$ and 3·55% CoO. Its textural properties are given in Table I. The catalyst was crushed to 0·16—0·25 mm size for which the internal diffusion effect can be neglected[1]. After filling the reactor, the catalyst was reduced in a stream of hydrogen at 773 K for 6 h. Between measurements, the catalyst was kept in the reactor in hydrogen stream. Prior to experiments, the catalyst was reactivated at 773 K. Each day, catalyst activity was checked by a run under standard conditions. For kinetic measurements, one catalyst charge was used for 4 days.

Apparatus. The apparatus is schematically shown in Fig. 1. Ethylene, hydrogen, ethane, and nitrogen pass through regulating valves **1** to gas purification **2**. The gas flow rate was measured by capillary flow meters **3**. Feed-streams of differing compositions were interchanged by four manually operated switching valves **4**. The reactor **5** is made of stainless steel and is partially filled with the catalyst. The stirring is ensured by vibrational movement of the reactor, the catalyst being fluidized and the reactor bulk being efficiently stirred[5]. The reactor temperature was controlled by a temperature controller and measured by a thermocouple (Fe–Ko) **7**. The reaction mixture composition in reactor outlet was analysed by gas chromatograph **8** with a thermal conductivity detector. The chromatographic conditions: stainless steel column (lenght 90 cm, i.d. 2 mm) packed with Spherocarb 80/100 mesh, column temperature 155°C. Hydrogen was

TABLE I

Textural properties of CHEROX 36—01 catalyst

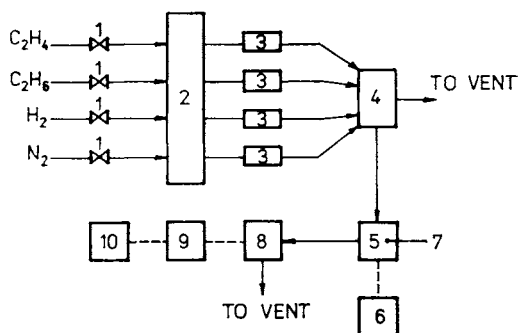|	
Specific surface (BET), m^2 g^{-1}	230
True density, g cm^{-3}	2·63
Apparent density, g cm^{-3}	1·16
Volume of pores, cm^3 g^{-1} with radii 7·5—7 500 nm	0·29
Most frequent pore radius, nm	109
Porosity	0·56

FIG. 1

Apparatus scheme

used as carrier gas; flow rate 65 cm^3 min^{-1}. The gas mixture was injected into the chromatograph by a sampling valve of special construction[6] which made it possible to collect samples in very short time intervals and stored them for analysis. The signal from thermal conductivity detector was transmitted to integrator **9** with printer **10**.

Adsorption and kinetic experiments. In adsorption measurements, adsorption properties of reaction components (ethylene, hydrogen and ethane) were followed separately. For each component, the response to step-replacement of nitrogen in the reactor feed by the same flow-rate of the component investigated was measured and then the response to the step-replacement of the component by nitrogen after the establishment of steady-state. The adsorption measurements were carried out at 353 K.

In kinetic measurements, ethylene of known feed-rate was step-added to the stream of hydrogen entering the reactor. After the steady-state attainment, the etylene stream was cut-off so that the reactor was flushed only with hydrogen. The reverse experiment, *i.e.* addition (and cut-off) of hydrogen to the ethylene stream, was not used since preliminary experiments showed that catalyst activity rapidly decreases in the absence of hydrogen. Kinetic measurements were carried out at 353 K for different ethylene/hydrogen molar ratios and for several W/F_E^0 values.

RESULTS AND DISCUSSION

Adsorption measurements were performed for all the components of the reaction mixture (ethylene, ethane, hydrogen) separately: the reactor response to step-interchange of nitrogen feed-stream for pure component feed-stream with identical F_i^0 was followed; after attainment of steady-state, the response to the reverse process, *i.e.* step-interchange of component feed-stream for nitrogen feed-stream, was followed as well. The transient response curves for ethylene, ethane, and hydrogen are shown in Fig. 2. The different shape of the curves indicates that ethylene is the substance adsorbed preferentially on catalyst surface. By contrast, the response for hydrogen is nearly the same as that for inert nitrogen, not adsorbed on the catalyst surface (the curve for nitrogen coincides with that for hydrogen in Fig. 2). The adsorption and desorption responses of ethane lie between those of ethylene and hydrogen, ethane being thus weakly adsorbed.

Qualitative conclusions concerning adsorption of individual components were confirmed by adsorbed concentrations, q_i (i = A, E, H), from balance equations (8)–(10). The source term $\int_0^{t_i} R_H\, dt$ is zero for adsorption experiments as no reaction takes place on the catalyst surface. The results of calculations are summarized in Table II. From numerical evaluation of transient response curves it follows that significant adsorption is observed only for ethylene, adsorption of ethane is weak, and adsorption of hydrogen — in agreement with earlier works[1,2] — is negligible.

In kinetic measurements, stream of ethylene of known volumetric feed-rate was step-added to steady feed-stream of hydrogen. After a new steady-state had been established, the ethylene feed-stream was cut-off. Conditions for kinetic experiments are summarized in Table III which presents also data on reaction rate r_s and hydrogen conversion x_{Hs} after steady state establishment. The steady-state conversion was

TABLE II

Results of adsorption experiments ($p_i = 100$ kPa)

Component, i	$q_{is} \cdot 10^2$, mmol g^{-1}
Hydrogen	0·079
Ethane	0·365
Ethylene	6·689

TABLE III

Results of steady-state kinetic measurements[a]

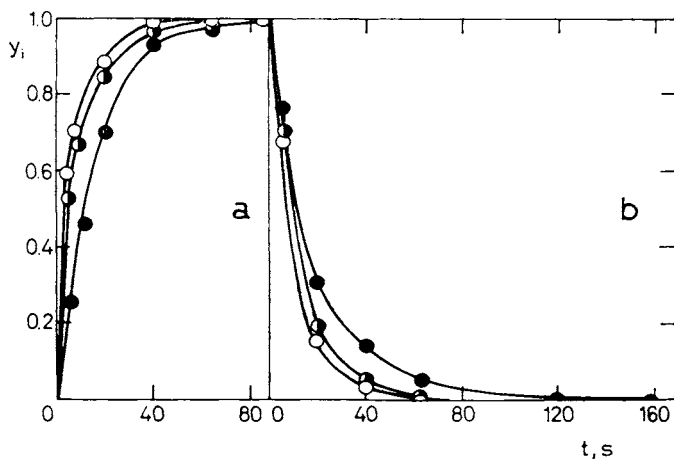| $W/F_H^0 \cdot 10^{-1}$ g s mmol^{-1}	y_H^0	y_E^0	x_{Hs}	$r_s \cdot 10^3$ mmol g^{-1} s^{-1}
4·6	0·50	0·50	0·82	17·7
19·5	0·20	0·80	0·92	4·7
11·5	0·35	0·65	0·93	8·1
9·4	0·50	0·50	0·89	9·5
5·8	0·50	0·50	0·86	14·8

[a] Reactor pressure 110 kPa.

FIG. 2

Composition response curves in adsorption (a) and desorption (b) measurements; $T = 353$ K, $F^0 = 1$ cm^3 s^{-1}, $W = 4·336$ g; ○ hydrogen, ◑ ethane, ● ethylene

calculated from the equation

$$x_{Hs} = 1 - (y_{Hs}/y_{Ho})(y_{Ho} - 1)/(y_{Hs} - 1) \qquad (11)$$

and reaction rate according to the relation

$$r_s = x_{Hs}/(W/F_H^0) . \qquad (12)$$

Examples of step-changes of feed composition and corresponding transient response curves are shown in Fig. 3. For determination of surface concentrations of reaction components, balance equations $(8)-(10)$ in combination with Eq. (5) were used, hydrogen being the key component. The shape of response curves shows that the transient period after ethylene addition is several times longer then after its cut-off. When compared to other terms of Eqs $(8)-(10)$, the terms $F_I^0 - \int_0^{t_\bullet} F y_i \, dt$, $i = A, E,$ H acquire values by a factor of ten higher. Therefore, determination of surface concentrations of adsorbed components would not be precise enough. For that reason, these concentrations were evaluated from material balances of the transient periods after ethylene stream cut-off. The solution of balance Eqs $(8)-(10)$, with the use of assumption (7) about negligible adsorption of hydrogen, proved the insignificant adsorption of ethane compared to ethylene, in accordance with results of adsorption experiments. The calculated surface concentrations of ethylene in steady-state, q_{Es}, are given in Table IV, along with corresponding partial pressures of ethylene, p_{Es}.

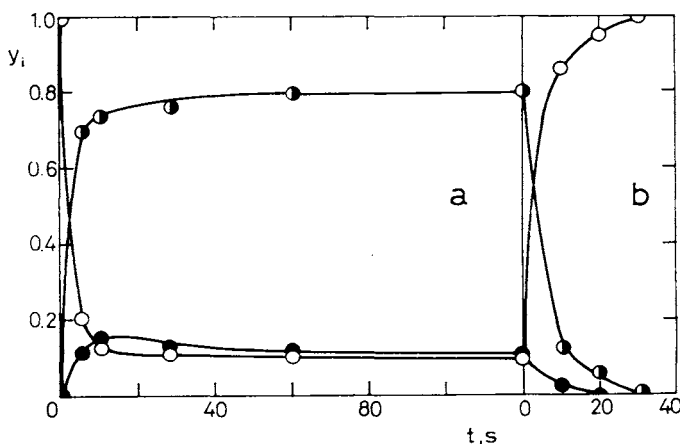FIG. 3

Composition response curves in a kinetic experiment; $\circ$ hydrogen, $\obullet$ ethane, $\bullet$ ethylene; a ethylene step-added to steady hydrogen stream ($y_H^0 = y_{Eo}^0 = 0.5$), b ethylene step-closed ($y_H^0 = 1$); $T = 353$ K, $W/F_H^0 = 46$ g s mmol^{-1}, $W = 4.301$ g

Provided that hydrogenation of ethylene proceeds according to the scheme

$$E + S \rightleftharpoons ES \qquad (13)$$

$$ES + H \rightarrow A + S, \qquad (14)$$

where S is the active site on catalyst surface, the rate of ethylene hydrogenation is expressed by the relation

$$r_s = kq_{Es}p_{Hs}. \qquad (15)$$

TABLE IV

Combined results of stationary and unsteady-state measurements

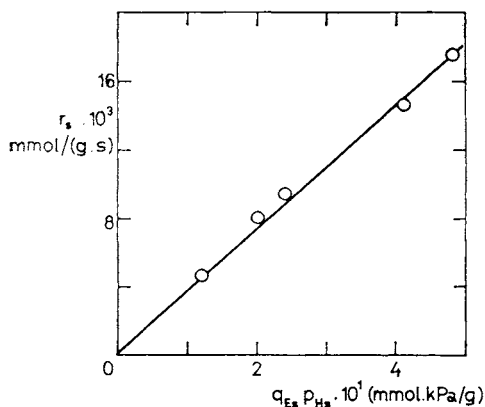| $r_s \cdot 10^6$ mol g^{-1} s^{-1}	p_{Hs} kPa	p_{Es} kPa	$q_{Es} \cdot 10^5$ mol g^{-1}
17·7	15·0	15·8	3·2
4·7	2·0	61·0	5·8
8·1	4·1	35·2	5·0
9·5	10·0	10·0	2·4
14·8	12·0	13·9	3·4

FIG. 4

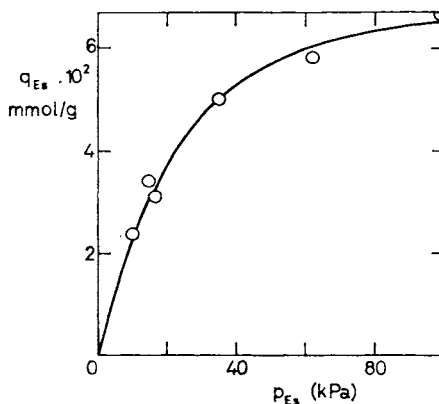Dependence of reaction rate, r_s, on the product $q_{Es}p_{Hs}$

FIG. 5

Adsorption isotherm of ethylene under reaction conditions; $T = 353$ K (the point $p_{Es} = 100$ kPa was obtained from adsorption experiment)

Steady-state rates, r_s, are listed in Table IV, along with corresponding hydrogen partial pressures, p_{Hs}. The validity of Eq. (15) and thus also of mechanism (13), (14) is documented by linear dependence of r_s on the product $q_{Es}p_{Hs}$ (Fig. 4). The rate constant of hydrogenation of ethylene at 353 K calculated from the slope of this linear dependence is $k = 3.6 \cdot 10^{-2} \text{ kPa}^{-1} \text{ s}^{-1}$.

The mechanism of ethylene adsorption (13) corresponds to the form of the adsorption isotherm

$$q_{Es} = LK_E p_{Es}/(1 + K_E p_{Es}).$$ (16)

By using the corresponding pairs q_{Es} and p_{Es} (Table IV), adsorption coefficient of ethylene $K_E = 4.7 \cdot 10^{-2} \text{ kPa}^{-1}$ and total concentration of active sites $L = 7.5 \cdot 10^{-5} \text{ mol g}^{-1}$ were calculated. The q_{Es} vs p_{Es} dependence calculated with these parameters is shown in Fig. 5. Total active sites concentration L corresponds to $2 \cdot 10^{17}$ Mo atoms per 1 m^2 of the catalyst. It was independently found by oxygen adsorption that for the CHEROX 36−01 catalyst this value lies between[7] $0.7 \cdot 10^{16}$ and $5 \cdot 10^{16}$ active Mo atoms *per* m^2. With regard to the relatively small set of treated experimental data, the agreement between results of both methods can be regarded as satisfactory.

Summarizing, hydrogenation of ethylene on the cobalt–molybdenum catalyst CHEROX 36−01 has been studied at 353 K and atmospheric pressure. The unsteady--state experimental technique was applied, in which feed-composition and feed-rate were changed in a controlled way. Responses of the catalytic system to these perturbances were determined experimentally as time profiles of composition of reaction components in the reactor outlet.

The qualitative and quantitative analysis of transient response curves confirmed that adsorption of hydrogen and ethane is negligible. Material balances for transient periods were used to evaluate surface concentrations of adsorbed ethylene under steady-state reaction conditions. Combination of unsteady- with steady-state data made it possible to verify the reaction mechanism of ethylene hydrogenation, involving reaction of adsorbed ethylene with hydrogen from gas phase in the rate determining step. The rate contant of the surface reaction has been determined $(k = 3.6 \cdot 10^{-2} \text{ kPa}^{-1} \text{ s}^{-1})$. The following quantities were calculated from the adsorption isotherm of ethylene: adsorption coefficient of ethylene $(K_E = 4.7 \cdot 10^{-2} \text{ kPa}^{-1})$, total active sites concentration $(L = 7.5 \cdot 10^{-5} \text{ mol g}^{-1})$, and concentration of active Mo atoms $(2 \cdot 10^{17}$ Mo atoms $m^{-2})$.

LIST OF SYMBOLS

a_i stoichiometric coefficient of component i
c total molar concentration
F total molar flow rate
F_i molar flow rate of component i

k	rate constant
K_i	adsorption coefficient of component i
L	total active sites concentration
p_i	partial pressure of component i
q_i	surface concentration of component i
r	reaction rate
R_i	rate of formation of component i
S	active site on catalyst surface
t	time
V	reactor free volume
W	catalyst weight
x	conversion
y	mole fraction of component i

Subscripts

i	for component ($i = $ A ethane, $i = $ E ethylene, $i = $ H hydrogen)
k	key component
o	steady state before the start of the transient period
s	steady state after the end of the transient period

Superscripts

0	reactor inlet

REFERENCES

1. Fott P., Schneider P.: This Journal *45*, 2742 (1980).
2. Jakubíčková E.: *Thesis*. Institute of Chemical Process Fundamentals, Czechoslovak Academy of Sciences, Prague 1979.
3. Klusáček K., Schneider P.: Chem. Eng. Sci. *37*, 1523 (1982).
4. Klusáček K.: This Journal *49*, 170 (1984).
5. Klusáček K., Schneider P.: Chem. Listy, in press.
6. Klusáček K., Schneider P., Masák V.: J. Chromatogr. *244*, 125 (1982).
7. Vyskočil V.: *Thesis*. Institute of Chemical Process Fundamentals, Czechoslovak Academy of Sciences, Prague 1978.

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